First Principles Modeling of Cluster-Based Solid Electrolytes

Puru Jena
Virginia Commonwealth University

June 24, 2021
2021 DOE Vehicle Technologies Office
Annual Merit Review

VCU

Project ID: BAT490

Overview

Timeline

- Project Start: Oct. 2019
- Project End: Dec. 2022
- Percent Complete: 40%

Budget

- Total project funding
  - DOE share: $793,040
  - Contractor share: $198,295
- FY 2020: $33,973.92

Barriers/Technical Targets

- Novel solid electrolytes
- New electrolytes with high transport numbers
- Electrolytes with wider temperature operating window for low T performance
- Understanding solid electrolytes and the interfaces

Partners

- Oak Ridge National Lab
- University of Texas Austin
- Ohio State University

VCU

Relevance

Impact

Novel solid electrolytes for high-performance battery systems for electric vehicles:

- High transport numbers
- Wide temperature operation window
- Good interfacial properties with electrodes are the key

Objectives

- Modeling development of cluster-based solid electrolytes
- Optimizing the transport and interfacial properties of the solid electrolytes by cluster-ions with different shapes, compositions and chemistries
- Fundamental understanding of the conduction mechanisms and interfacial performance
- Guiding experimental synthesis and implementation in cells

VCU

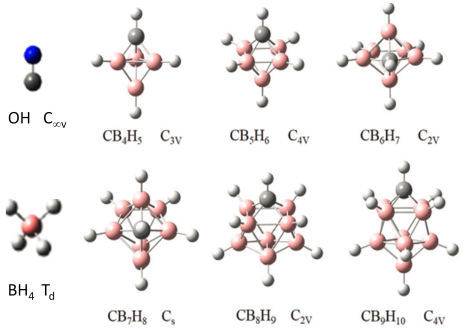
Milestones

Time	Type	Description
FY 2020	Technical	➢Structural studies of the designed cluster-based solid electrolyte materials.(Complete) ➢Characterizations of the cluster-based solid electrolyte materials.(Complete) ➢Ionic conductivity characterization of the solid electrolytes and mechanisms.(Complete)
	Go/No Go	➢Development of cluster-based solid electrolyte materials with a database.(Complete)
Jan. – Dec. 2021	Technical	➢Structural studies of chemically mixed systems with both cluster- and atomic ions.(Complete) ➢Ionic conductivity and relevant property characterizations of the chemically mixed systems.(On schedule) ➢Cation doping in the cluster-based solid electrolyte systems.(On schedule)
	Go/No Go	➢Modeling and optimizing the chemical mixing and cation doping.(On schedule)
Jan. – Dec. 2022	Technical	➢Phase analysis between the cluster-based solid electrolyte and electrodes.(On schedule) ➢Studying the structural, chemical/electrochemical, and transport properties of interfaces.(On schedule) ➢Identifying potential coating materials and modeling the interfaces.(On schedule)

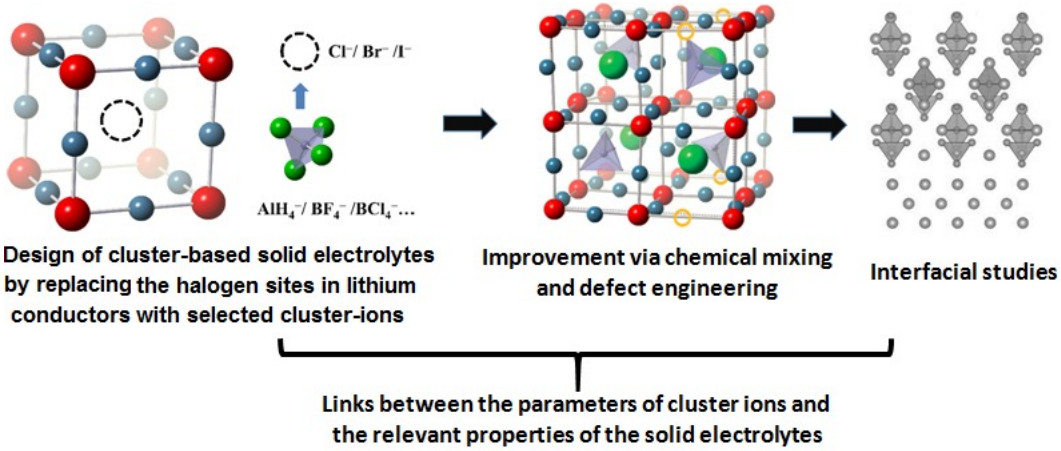
VCU

Approach

Cluster-ions with different compositions, sizes, shapes, electron affinities, etc. can provide additional degrees of freedom to tune the bulk properties of materials



Mono-anion	Radius (Å)	EA (eV)
CN^-	1.401	4.10
Cl^-	1.810	3.62
Br^-	1.960	3.36
I^-	2.200	3.06
BH_4^-	2.239	3.42
AlH_4^-	2.645	4.03
BF_4^-	2.747	7.33
ClO_4^-	2.901	5.36
SCN^-	3.077	3.50
$CB_6H_7^-$	3.354	3.73
$CB_4H_5^-$	3.354	2.90
$B_7H_7^-$	3.380	2.25
$CB_5H_6^-$	3.401	3.74
$B_6H_6^-$	3.436	3.03
$CB_7H_8^-$	3.446	3.44
$B_8H_8^-$	3.501	3.15
$B_5H_5^-$	3.521	2.40
$B_9H_9^-$	3.544	3.23
$CB_8H_9^-$	3.562	3.67
BCl_4^-	3.693	5.01
$CB_{11}H_{12}^-$	3.753	5.37
$CB_9H_{10}^-$	3.903	4.45
$B_{10}H_{10}^-$	4.052	3.68



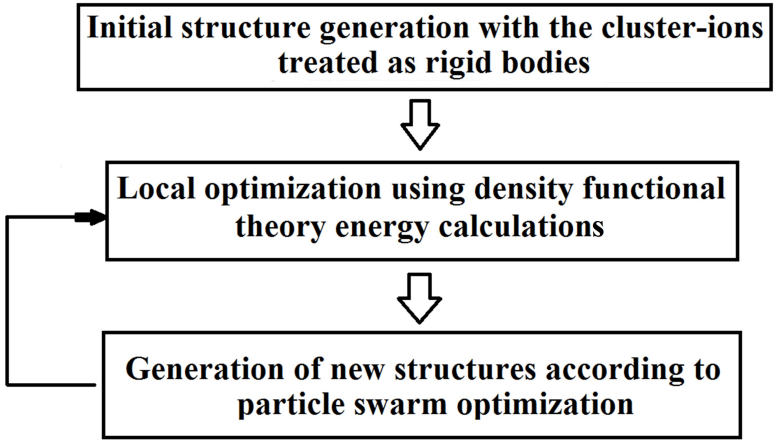
- **Structure search based on Particle Swarm Optimization and density functional energy (DFT) calculations, with the cluster-ions treated as rigid-bodies in the initial structure.**
- **Characterizing and understanding the cluster-based solid electrolytes and its chemically/defect engineered derivatives using DFT calculations, molecular dynamics simulations, various models (e.g., electrostatic, phenomenological and phase-analysis models), as well as machine learning.**

VCU

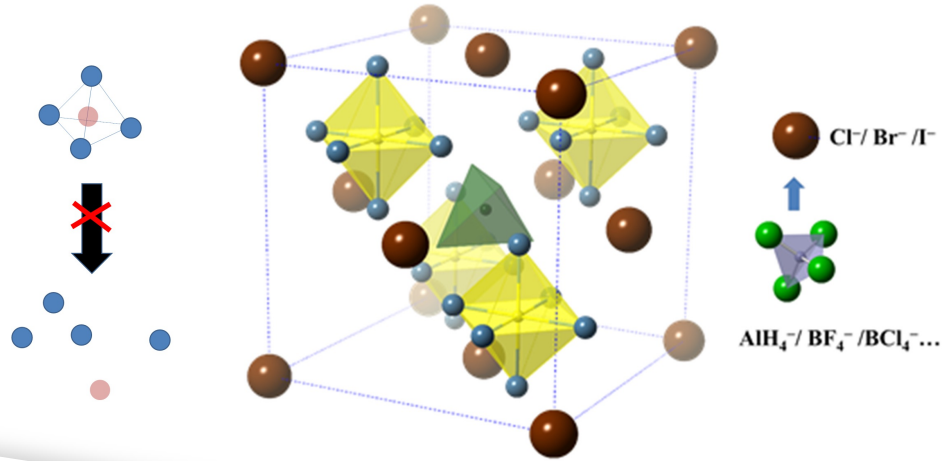
Technical Accomplishments and Progress

Technical milestone (Jan/2020): Structural study of the cluster-based solid electrolytes

Key steps in the structure search procedure

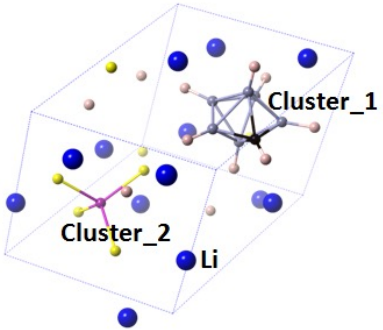


A cluster-ion is treated as a rigid body, instead of individual atomic species, in the generated initial structure. For example, the halogen sites in the argyrodite lithium conductor are substituted by cluster-ions.

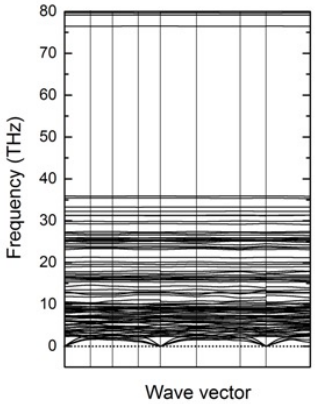


Technical milestone (Jun/2020): Properties of the cluster-based solid electrolytes

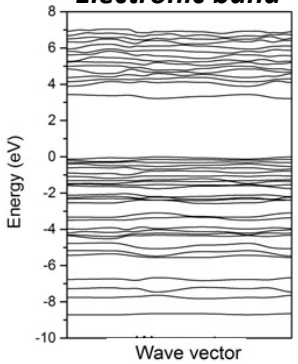
Crystal Structure



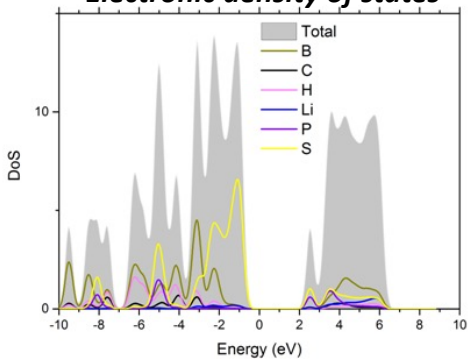
Phonon



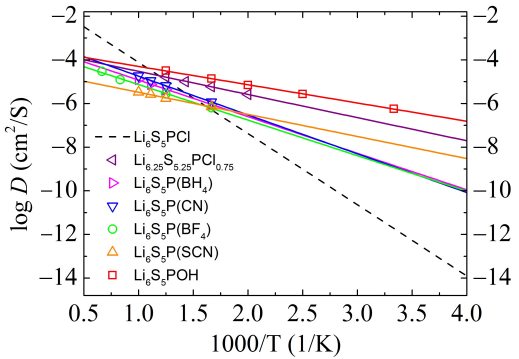
Electronic band

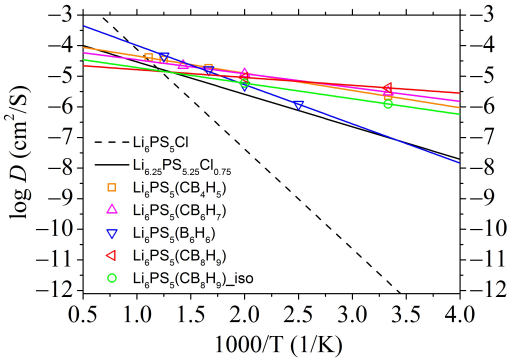


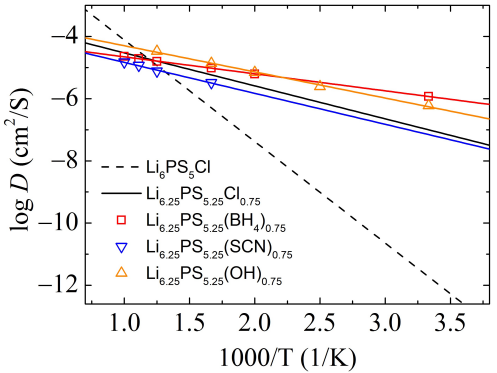
Electronic density of states

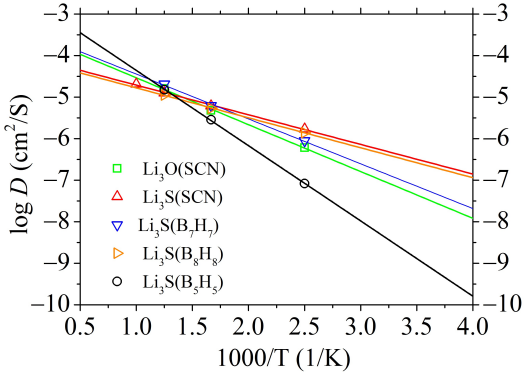


Calculated diffusivities at different temperatures fitted by the Arrhenius relation for each electrolyte



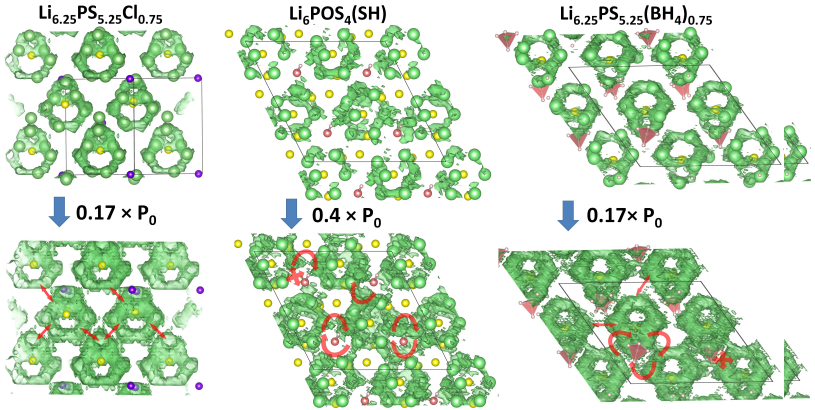




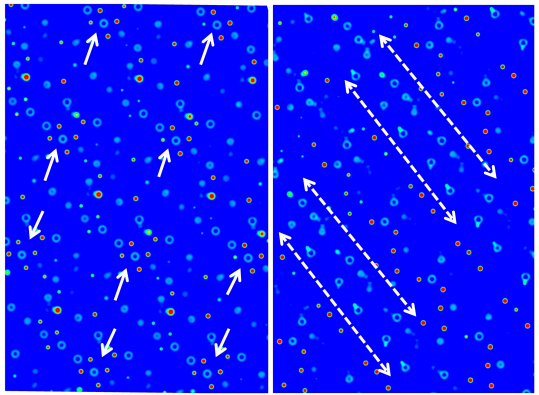


Technical milestone (Sep/2020): Fundamental understanding of the fast-ion diffusion

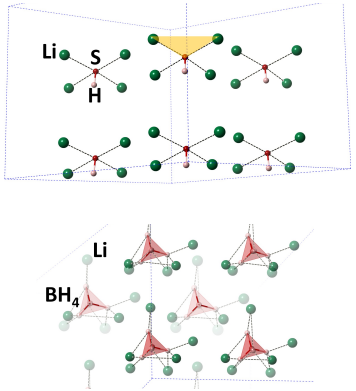
Probability distribution function to show the Li-conducting pathways



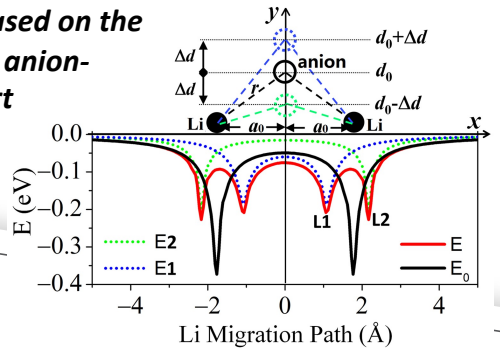
Charge density map to show the rotor phase of cluster-ions upon thermal excitation



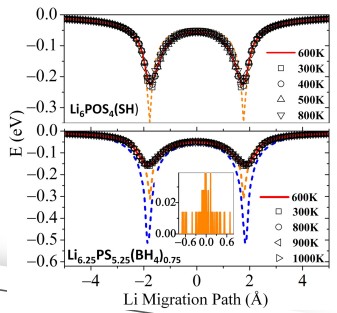
Topology characterizations for the materials



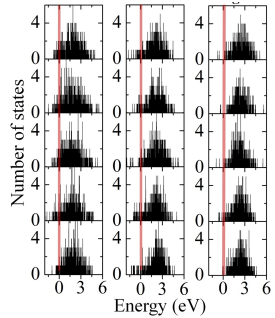
Established model based on the local topology of the anion-mediated Li-transport



Modeling and understanding the activation energy of the materials



Method to evaluate the 'free-ion' energy states for Li-ions in the material



Milestone (Dec/2020): Database of the cluster-based solid electrolytes

Table Cluster-ion based structures studied as candidates for electrolytes of lithium superionic conductors. "EA" stands for electron affinity of the cluster-ion. Band gaps are in eV. "Z" stands for the number of formula units in the unit cell. "S" means lattice dynamically stable and "INS" means instable. "C" means electrical conducting. "IC" is the calculated ionic (Li^+) conductivity at room temperature. "E_a" is the activation energy.

Material	Tolerance Factor	Z	Lattice Dynamics	Bandgap	IC (mS/cm)	E_a (eV)
$Li_3O(SCN)$ $Li_3S(SCN)$	1.015 0.844	1	S	2.50 3.08	11 62	0.224 0.142
$Li_3S(CB_6H_7)$[a]	1.157	1	S	2.97	928 (800 K)	--
$Li_3S(CB_4H_5)$	1.157	1	S	3.34	531 (600 K)	--
$Li_3S(B_7H_7)$	1.164	1	S	C	9.8	0.214
$Li_3S(CB_5H_6)$	1.170	1	S	3.52	0.0	--
$Li_3S(B_6H_6)$[a]	1.179	8	S	3.45	412 (500 K)	--
$Li_3S(CB_7H_8)$[a]	1.182	1	S	2.86	1185 (800 K)	--
$Li_3S(B_8H_8)$	1.197	1	S	C	30	0.143
$Li_3S(B_5H_5)$	1.202	8	S	1.40	0.38	0.360

[a] Calculations show that these materials exhibit little fast-ion conductivities at room temperature. In each of these cases, the Li^+ conductivity corresponds to the value at the simulated temperature specified in the parenthesis. The activation energy from the Arrhenius relationship is, therefore, unavailable.

Table Cluster-ion based structures studied as candidates for electrolytes of lithium superionic conductors. A well-known typical argyrodite solid electrolyte Li_6PS_5Cl is listed for comparison. "EA" stands for electron affinity of the cluster-ion. Band gaps are in eV. "Z" stands for the number of formula units in the unit cell. "S" means lattice dynamically stable and "INS" means instable. "C" means electrically conductive. "IC" means the calculated ionic conductivity at room temperature. "E_a" means the activation energy.

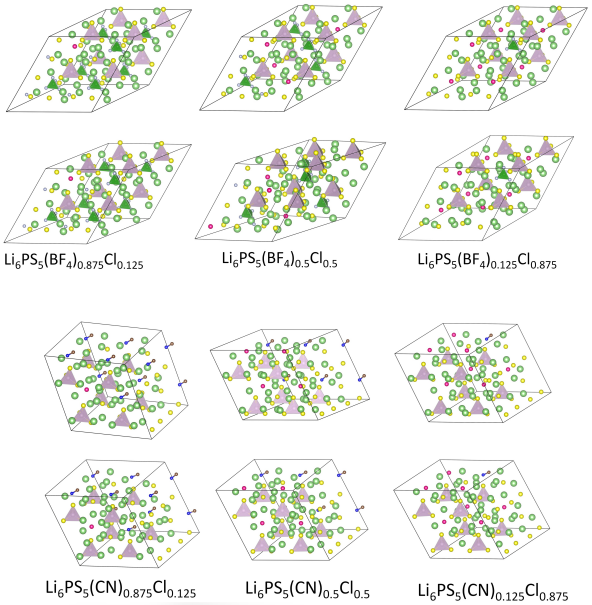
Material	Structure Identified	Z	Lattice Dynamics	Bandgap	IC (mS/cm)	E_a (eV)
Li_6PS_5Cl	○	4	S	3.4 (HSE)	0.25×10^{-3}	0.647
$Li_{6.25}PS_{5.25}Cl_{0.75}$	Nonstoichiometric Li_6PS_5Cl with Li-excess actually synthesized in the experiment				14	0.210
$Li_6PS_5(CN)$	○	1	S	3.22 (HSE) 2.14 (mBJ)	0.18	0.353
$Li_6PS_5(OH)$	●	1	S	4.37 (HSE) 3.18 (mBJ)	82	0.166
$Li_{6.25}PS_{5.25}(OH)_{0.75}$	Nonstoichiometric configuration with Li-excess				51	0.183
$Li_6PS_5(SCN)$	○	1	S	3.40 (HSE) 2.22 (mBJ)	1.9	0.201
$Li_{6.25}PS_{5.25}(SCN)_{0.75}$	Nonstoichiometric configuration with Li-excess				10	0.197
$Li_6PS_5(BH_4)$	○	1	S	3.47 (HSE) 2.25 (mBJ)	0.20	0.333
$Li_{6.25}PS_{5.25}(BH_4)_{0.75}$	Nonstoichiometric configuration with Li-excess				177	0.108
$Li_6PS_5(BF_4)$	○	1	S	3.50 (HSE) 2.41 (mBJ)	0.15	0.323
$Li_6PS_5(CB_6H_7)$	○	1	S	4.39 (HSE) 3.21 (mBJ)	296	0.090
$Li_6PS_5(CB_4H_5)$	○	4	S	2.66 (mBJ)	235	0.112
$Li_6PS_5(B_7H_7)$	●	4	S	2.32 (mBJ)	melting	
$Li_6PS_5(CB_5H_6)$	○	1	S	4.20 (HSE) 3.05 (mBJ)	78	--
$Li_6PS_5(B_6H_6)$	●	1	S	C	11	0.254
$Li_6PS_5(CB_7H_8)$	○	1	INS	—	--	--
$Li_6PS_5(B_8H_8)$	●	8	INS	—	--	--
$Li_6PS_5(B_9H_9)$	○	8	INS	—	--	--
$Li_6PS_5(CB_8H_9)$	●	1	S	2.99 (HSE) 1.85 (mBJ)	103	0.101
$Li_6PS_5(CB_8H_9)$	○	2	S	3.96 (HSE) 2.87 (mBJ)	310	0.051

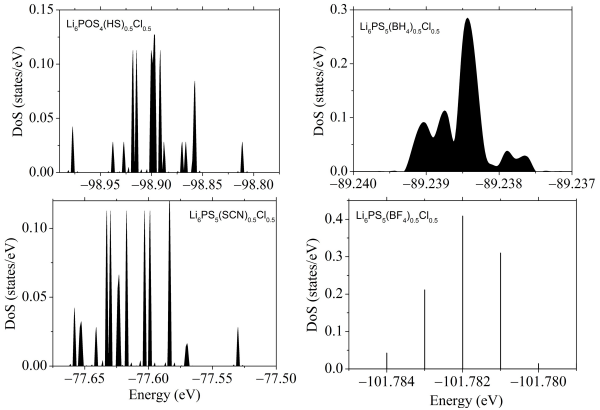
○The cluster-ion remains in the lowest-energy structure.
●The cluster-ion partially reacts with PS_4^{3-} in the lowest-energy structure. One hydrogen in $B_xH_x^-$ is replaced by S and $B_xH_{x-1}S^{2-}$, HS^- and PS_3^{3-} are formed in the structure.
—The cluster-ion is highly distorted or disintegrated in the lowest-energy structure.

VCU

Technical Milestone (Mar/2021): Structural study for the chemically mixed systems

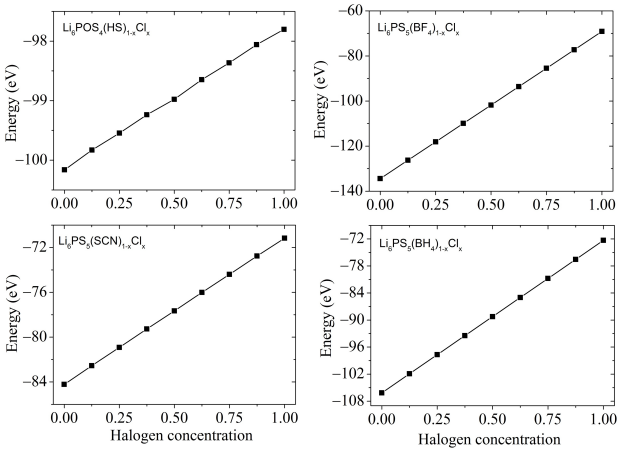
Identified ground-state configurations with different chemical-mixing concentrations according to a point-charge electrostatic model vs. DFT optimization.





Density of states shows that all possible combinations of substitutional sites in a structure are considered for a specific chemical-mixing concentration and the energy of each combination is computed based on a point-charge electrostatic model of the material. Configurations contained in the lowest-energy peak are subject to further DFT optimizations to identify the ground state.

Total energy of the chemically mixed structure is found to be increasing linearly with the increasing concentration of the cluster-ions being substituted by atomic ions.



Responses to Previous Year Reviewers' Comments

- This is the first year that the project has been reviewed.

Collaboration and Coordination

Oak Ridge National Lab (J. Nanda and team): solid electrolyte synthesis and characterization; cell implementation.

University of Texas Austin (D. Mitlin and team): solid electrolyte synthesis and characterization; cell implementation.

Ohio State University (Y. Wu and team): solid electrolyte synthesis and characterization; cell implementation.

Remaining Challenges and Barriers

Modeling and optimizing the interfacial properties between the cluster-based solid electrolytes and the electrodes, especially with lithium metal anode:

- Large-scale simulations to study the kinetics at the interfaces (using on-the-fly force-field model obtained from machine learning techniques)
- Electrochemical instability of the solid electrolytes with the electrodes (identifying candidates as buffer materials)

Synthesizing and characterizing the cluster-based solid electrolytes in practice:

- Solid electrolyte materials with high ionic conductivities at room temperature are thermodynamically meta-stable (exploring different synthetic routes)
- Properties of the solid electrolytes in practice are limited by preparation quality of sample, grain boundaries, etc. (close collaborating with the experimental group to reach optimized performance of the material)

VCU

Proposed Future Research

Chemical and defect engineering on the developed cluster-based solid electrolytes to achieve optimized properties (now-Dec. 2021):

- Property characterizations for the chemically-mixed systems with different concentrations of the cluster-ions
- Structural and property characterizations for the cation (multi-valence) doped lithium systems with different concentrations

Interfacial studies (Jan.-Dec. 2022):

- Phase and electrochemical stability analysis at the interfaces between the cluster-base solid electrolytes and electrodes including the Li metal anode
- Direct simulations to study the ion kinetics and transport properties at the interfaces
- Buffer materials at the interfaces

VCU

Any proposed future work is subject to change based on funding levels

Summary

Achievements:

- Database of cluster-based solid electrolytes
- New mechanistic principles and design rules to achieve solid electrolytes with high ionic conductivities at room temperature and low activation energies

Technical highlights:

- Taking advantage of the additional degrees of freedom introduced by the cluster-ions (e.g., different sizes, shapes, compositions, internal charge distributions, etc.) to tune and optimize the bulk properties of solid electrolytes
- New physical models as well as computational codes and methods developed to study and understand the fast-ion diffusion in the solid electrolytes and their chemically-mixed derivatives.

Impact toward VTO objectives:

- Design and characterize of novel solid electrolytes having high transport numbers and wide operative temperature range
- Fundamental understanding of the fast-ion diffusion and interfacial optimization to guide high-performance battery systems in practice

VCU